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(54) Title: RADIATION CURABLE RESIN COMPOSITION

(57) Abstract

A radiation curable resin composition suitable for use as a primary coating material for optical fibers, which can form a cured coating with a low modulus of elasticity exhibiting a high breaking strength, and small light transmission loss; the coating composition comprises (A) a polymer containing polymerizable unsaturated groups in an average amount of 1.2 per molecule, a urethane bond in a molecular chain, and having a number average molecular weight from 3,000 to 30,000, (B) a poly-functional monomer having two or more polymerizable unsaturated groups, (C) a monomer having one polymerizable unsaturated group, and (D) a radiation active initiator. The secant modulus of the coating is less than 0.15 kg/mm², the tensile strength is more than 0.15 kg/mm².

↓

102(b) 1.4 MPa
1, 4, 7, 9, 11, 12, 13

102(b) / 103(a)

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RADIATION CURABLE RESIN COMPOSITION

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Field of the Invention

The present invention relates to a radiation curable resin composition, and particularly to a radiation curable resin composition suitable for 10 use as a coating material for optical fibers.

Description of related art

Because optical fibers are fragile and easily broken, the optical fibers are usually coated 15 with a coating material which is a radiation curable resin composition. The transmission characteristics of optical fibers are known to be significantly affected by properties such as modulus of elasticity or the like of the primary coating material which is in direct 20 contact with the optical fibers. Because the primary coating material absorbs a high lateral pressure, materials having a modulus of elasticity of 0.15 kg/mm² or less, in terms of a secant modulus measured by JIS K 7127, have conventionally been used.

25

Problems to be Solved by the Invention

In spite of the excellent transmission characteristics due to the low modulus of elasticity, such a conventional radiation curable resin composition 30 has a drawback when used as the primary coating material for optical fibers. That is, when the primary

coating material is removed to connect an optical fiber with another optical fiber, a portion of resinous material is left on the optical fibers. The complete removal of such resinous material remaining requires 5 time-consuming procedures, impairing the processability of the material.

Accordingly, one object of the present invention is to provide a radiation curable resin composition suitable for use as a primary coating 10 material for optical fibers, which can form a cured coating with a low modulus of elasticity exhibiting a high breaking strength and small light transmission loss, and yet easily removed from optical fibers.

15 Means for Solving the Problems

The above-described object can be achieved in the present invention by a radiation curable resin composition comprising:

(A) a polymer containing polymerizable 20 unsaturated groups in an average amount of 1.2 per molecule, a urethane bond in a molecular chain, and having a number average molecular weight from 3,000 to 30,000,

(B) a poly-functional monomer having two or more 25 polymerizable unsaturated groups,

(C) a monomer having one polymerizable unsaturated group, and

(D) a radiation active initiator.

which can produce a cured product with a secant modulus 30 of 0.15 kg/mm² or less and a tensile strength of 0.15 kg/mm² or more when cured by ultraviolet radiation at a

1.4 MPa

dose of 1 J/cm² in air.

The above object is preferably achieved in the present invention by the radiation curable resin composition, which can produce a cured product having a 5 total of at least two peaks or shoulders in a temperature range from -50°C to +35°C, preferably at least one peak or shoulder in a temperature range from -50°C to -20°C and at least one peak or shoulder in a temperature range from -20°C to +35°C, in a temperature 10 dependency curve of loss tangent obtained from a temperature dependency measurement of a dynamic viscoelasticity ratio when cured by ultraviolet radiation at a dose of 1 J/cm² in air.

Preferably the composition comprises:

15 (A) 25 to 75 wt% of a polymer containing polymerizable unsaturated groups in an average amount of 1.2 per molecule, a urethane bond and a polyoxyalkylene structure in a molecular chain, and having an average molecular weight from 3,000 to 20 30,000,

(B) 0.1 to 10 wt% of a poly-functional monomer having 2 to 6 polymerizable unsaturated groups,

(C) 20 to 70 wt% of a monomer having a molecular weight from 100 to 650 and having one polymerizable 25 unsaturated group, and

(D) 0.1 to 10 wt% of a radiation-active initiator.

BRIEF DESCRIPTION OF THE DRAWINGS

30 Figure 1 shows a temperature dependency curve of loss tangent (plotted figure) of the cured

product produced from the composition of Example 3.

Figure 2 shows a temperature dependency curve of loss tangent (plotted figure) of the cured product produced from the composition of obtained in
5 Comparative Example 2.

Detailed description of the invention

The composition of the present invention will now be described in detail.

10 The following words used in the present specification have the meanings defined below:

In a temperature dependency curve of loss tangent, the word "peak" means an apex of a convex curve in a limited area and "shoulder" means a shoulder
15 or step in the same curve. A shoulder is present in the loss tan δ curve in case the derivative of the loss tangent curve shows a peak.

"(meth)acrylic acid" means acrylic acid and methacrylic acid inclusively.

20 "(meth)acryloyl group" means acryloyl group and methacryloyl group inclusively.

"(meth)acrylate" means acrylate and methacrylate inclusively.

25 Component (A)

The polymer used as the component (A) (hereinafter may also be called polymer (A)) has polymerizable unsaturated groups in an average amount of 1.2 per one molecule, a urethane bond in the
30 molecular chain, and a number average molecular weight from 3,000 to 30,000.

In this specification, the polymerizable unsaturated group is a radically polymerizable ethylenically unsaturated group such as, for example, a (meth)acryloyl group. The average number of 5 polymerizable unsaturated groups in the polymer (A) is 1.2 or more, preferably 1.2-4, and more preferably 1.5-2.5. Although an individual molecule of the polymer in the component (A) may have one or more polymerizable unsaturated groups, the average number of such a group 10 per molecule should be 1.2 or more. If the average number of polymerizable unsaturated groups per molecule is less than 1.2, the resulting composition exhibits inadequate curability. If the average number of the polymerizable unsaturated groups is more than 4, on the 15 other hand, the cross-linking reaction becomes excessive, resulting in brittle cured products.

The polymer (A) has a number average molecular weight of 3,000-30,000, and preferably 5,000-20,000. When the number average molecular weight is 20 less than 3,000, cured products obtained from the composition tend to have poor elongation and low tenacity. When used as a coating material for the optical fibers, such a composition may result in a transmission loss of optical fibers. If the number 25 average molecular weight is greater than 30,000, viscosity of the composition is excessively high so that the composition can be handled only with difficulty.

The polymer (A) contains an average of 1.2 30 or more, preferably 1.5-10, and more preferably 2-6, urethane bonds in a molecular chain. If the average

number of urethane bonds is less than 1.2, tenacity of the cured products produced from the composition is poor. Such a composition tends to result in transmission loss when used as a coating material for 5 optical fibers.

Although the polymer (A) must have a limited number of polymerizable unsaturated groups, a limited number of urethane bonds, and a limited average molecular weight as mentioned above, the structure of 10 the main chain may comprise, for example, a polyether polyol urethane polymer, polyester polyol urethane polymer, polycaprolactone polyol urethane polymer, and the like. Either one type of these polymers may be used or two or more types may be used in combination in the 15 polymer (A). Of these polymers for the structure of the main chain, comprising a polyether polyol urethane polymer is preferred. Either the entire main chain is formed from the polyether polyol urethane polymer or a portion of the main chain is formed from the polyether 20 polyol urethane polymer.

The polymer of the component (A) which has such a polyether polyol-type urethane polymer as a basic structure can be prepared by reacting (a) a polyether polyol obtained by the ring-opening 25 polymerization of an alkylene oxide (hereinafter referred to polyether polyol (a)), (b) a polyisocyanate (hereinafter polyisocyanate (b)), and (c) a compound possessing an active hydrogen reactive with an isocyanate group and a polymerizable unsaturated group 30 (hereinafter compound (c)).

The polyether polyol (a) is a polyol,

preferably a diol, having a polyoxyalkylene structure containing an oxyalkylene group with 2-10 carbon atoms as a repeating unit.

Given as examples of the diols having such a polyoxyalkylene structure are polyglycol compounds such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyheptamethylene glycol, polyhexamethylene glycol, and polydecamethylene glycol, as well as polyether diols obtained by a ring-opening copolymerization of two or more ion-polymerizable cyclic compounds.

The following cyclic diols are given as examples of the ion-polymerizable cyclic compound: ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, 3,3-bis(chloromethyl)oxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrin, glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyltetrahydrofuran, vinylcyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidyl ester of benzoic acid.

In addition, polyether diols obtained by the ring-opening copolymerization of the above-mentioned ion-polymerizable cyclic compound and a cyclic imine such as ethyleneimine, a cyclic lactone such as p-propyolactone, a cyclic lactone such as glycolic acid lactide, or a cyclic siloxane such as dimethylcyclopolsiloxane can also be used.

As specific combinations of two or more above-mentioned ion-polymerizable cyclic compounds, combinations of tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, 5 tetrahydrofuran and 3-methyltetrahydrofuran, tetrahydrofuran and ethylene oxide, and propylene oxide and ethylene oxide can be given. These two or more ion-polymerizable cyclic compounds may be bonded randomly in the resulting ring-opening copolymer.

10 The diols having such a polyoxyalkylene structure can be commercially available under the trademarks of, for example, PTMG1000 (Mitsubishi Chemical Corp.), PTMG2000 (same), PPG1000 (Asahi Oline Co., Ltd.), PPG2000 (same), EXCENOL2020 (same), 15 EXCENOL1020 (same), PEG1000 (Nippon Oil and Fats Co., Ltd.), Unisafe DC 1100 (same), Unisafe DC 1800 (same), PPTG2000 (Hodogaya Chemical Co., Ltd.), PPTG1000 (same), PTG400 (same), and PTGL2000 (same).

20 A diol and/or diamine which do not have a polyoxyalkylene structure may be used jointly with the polyether polyol (a) in the manufacture of the polyether polyol urethane polymer used as the component (A). Here, as examples of the diol which does not have a polyoxyalkylene structure, a polyester diol, 25 polycaprolactone diol, polycarbonate diol, and the like can be given. As examples of the polyester diol, polyester diols obtained by the reaction of a polyhydric alcohol, such as ethylene glycol, propylene glycol, tetramethylene glycol, 1,6-hexanediol, 30 neopentyl glycol, or 1,4-cyclohexanedimethanol, and a polybasic acid, such as phthalic acid, isophthalic

acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, or sebacic acid, can be given. As the polycaprolactone diol, polycaprolactone diols obtained by reacting ϵ -caprolactone and a diol such as ethylene

5 glycol, tetramethylene glycol, 1,6-hexanediol, neopentyl glycol, or 1,4-butanediol can be given. As examples of the polycarbonate diol, a polycarbonate diol of polytetrahydrofuran, a polycarbonate of 1,6-hexanediol, as well as products commercially available

10 under the trademarks of DN-980 (Nippon Polyurethane Industry Co., Ltd.), DN-981 (same), DN-982 (same), DN-983 (same), PC-8000 (PPG Co. of the U.S.), and the like can be given. As examples of the above-mentioned diamines, diamines such as ethylenediamine,

15 tetramethylenediamine, hexamethylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylmethane, diamines including a hetero-atom, polyether diamines, and the like are given.

The polyisocyanate (b) is a compound having

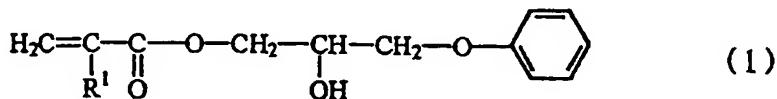
20 2 to 6 isocyanate groups. Usually diisocyanate compounds are used. Specific examples of the diisocyanate compounds include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate,

25 1,5-naphthalene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, hexamethylene diisocyanate, isophorone

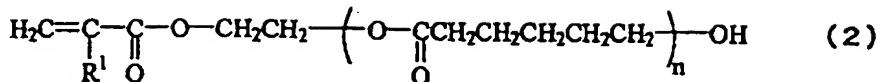
30 diisocyanate, dicyclohexyl methane diisocyanate, methylenebis(4-cyclohexylisocyanate), hydrogenated

diphenylmethane diisocyanate,
2,2,4-trimethylhexamethylene diisocyanate,
bis(2-isocyanateethyl)fumarate, 6-isopropyl-1,3-phenyl
diisocyanate, 4-diphenylpropane diisocyanate, lysine
5 diisocyanate, and the like. It is preferred to use
isophoronediisocyanates or another aliphatic
isocyanate.

As examples of the foregoing compound (c)
having an active hydrogen and polymerizable unsaturated
10 group, (meth)acrylic compounds having a hydroxyl group
are given. Specific examples are (meth)acrylates such
as 2-hydroxyethyl (meth)acrylate, 2-
hydroxypropyl (meth)acrylate,
2-hydroxyoctyl (meth)acrylate,
15 pentaerythritoltri (meth)acrylate,
glyceroldi (meth)acrylate,
dipentaerythritolmonohydroxypenta (meth)acrylate,
1,4-butanediolmono (meth)acrylate,
4-hydroxycyclohexyl (meth)acrylate,
20 1,6-hexanediolmono (meth)acrylate,
neopentylglycolmono (meth)acrylate,
trimethylolpropanedi (meth)acrylate, and
trimethylolethanedi (meth)acrylate, as well as
(meth)acrylates shown by the following formulas (1) or
25 (2):



wherein R^1 is a hydrogen atom or methyl group,



wherein R^1 is the same as in the formula (1) and n is an integer of 1 to 5.

2-Hydroxyethyl (meth)acrylate can be given as a preferred compound among these (meth)acrylates.

Moreover, compounds which do not have an active hydrogen nor a polymerizable unsaturated group can be given as compound (c'). Specific examples are silane coupling agents such as γ -mercaptopropyltrimethoxysilane, γ -aminopropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, and alcohols such as methanol, isopropyl alcohol, ethanol, and butanol. An alcohol is used to replace polymerizable unsaturated groups of the component (A) with non-polymerizable groups. This can decrease the cross-linking degree of the cured products and, accordingly, the modulus of elasticity of the product. The silane coupling agents can be used not only for lowering the modulus of elasticity of the cured products, but also for increasing adhesion strength between the cured products and glass, or for making the surface of cured products slippery.

The reaction of the polyether polyol (a), polyisocyanate (b), and compound (c), for example, the reaction of a diol compound, a diisocyanate compound, and a compound having an ethylenically unsaturated group can be preferably carried out using a urethanization catalyst such as copper naphthenate,

cobalt naphthenate, zinc naphthenate, dibutyl tin dilaurate, triethylamine, 1,4-diazabicyclo[2.2.2]octane, or 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane in an amount of 0.01-1 part
5 by weight for 100 parts by weight of the reaction components. The reaction is carried out at a temperature usually of 10-90°C, and preferably 30-80°C.

As mentioned above, inclusion of a polyether polyol-type urethane polymer in the polymer 10 of the component (A) is desirable. The component (A) may consist only of a polyether polyol-type urethane polymer or may contain a polyether polyol-type urethane polymer as a major component combined with other polymers belonging to the component (A). As examples of 15 other polymers belonging to the component (A), polyester polyol-type urethane polymer, polycaprolactone polyol-type urethane polymer, and the like can be given. When such other polymers are used together with polyether polyol-type urethane polymers 20 at the same time, the proportion of a polyoxyalkylene structure contained in the component (A) is preferably 50-98 wt%, more preferably 60-93 wt%, and most preferably 70-90 wt%. If the amount of the polyoxyalkylene structure in the component (A) is too 25 small, the modulus of elasticity of the cured products increases at a low temperature, for example at a temperature less than 0°C. This tends to produce a transmission loss of optical fibers when the composition is used as a coating material for optical 30 fibers.

The proportion of the component (A) in the

composition of the present invention is usually 25-75 wt%, and preferably 40-70 wt%. If the proportion of the component (A) is too small, the elongation of the cured products is decreased; if too large, the viscosity of 5 the composition increases. Handling of the material is impaired in either case.

Component (B)

Poly-functional monomers used as the 10 component (B) of the present invention have two or more, usually 2-10, and preferably 2-6, polymerizable unsaturation groups. A (meth)acryloyl group is desirable as the polymerizable unsaturation group.

It is desirable for the composition of the 15 present invention to contain a poly-functional monomer having a relatively low molecular weight for producing cured products with a high breaking strength, while exhibiting a low modulus of elasticity. Specifically, such a poly-functional monomer should have a molecular 20 weight of less than 800, preferably 70-800, and more preferably 100-650. The following compounds can be given as such preferable poly-functional monomers: trimethylolpropane tri(meth)acrylate, pentaerythritol(meth)acrylate, ethylene glycol 25 di(meth)acrylate, tetraethylene glycol di(meth)acrylate, di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 30 trimethylolpropanetrioxethyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate,

tris(2-hydroxyethyl) isocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, epoxy(meth)acrylate produced by the addition of (meth)acrylate to diglycidyl ether of bisphenol A, and 5 3-methyl-1,5-pentanediol diacrylate. Of these, 1,6-hexanedioldiacrylate, 1,9-nananediolacrylate, triethylene glycol diacrylate, tricyclodecanedimethanol diacrylate, and trimethylolpropane alkoxy triacrylate are desirable poly-functional monomers in view of the 10 low modulus of elasticity and high breaking strength of the resulting cured products. Particularly preferred polyfunctional monomers are 1,6-hexanedioldiacrylate, 1,9-nananediolacrylate, triethylene glycol diacrylate, and tricyclodecanedimethanol diacrylate. 15 These monomers may be used either individually or in combinations of two or more as the component (B).

These poly-functional monomers are commercially available under the trademarks of, for example, HDDA, L-C9A (Daiichi Kogyo Seiyaku Co., Ltd.), 20 Yupimer UV, SA1002, SA2007 (Mitsubishi Chemical Corp.), 3-EGA, 4-EGA, 9-EGA, 14-EGA (Kyoeisha Chemical Co., Ltd.), PHOTOMER4149 (Sunnopco Co., Ltd.), Viscoat 700 (Osaka Organic Chemical Industry Co., Ltd.), KAYARAD R-604, DPCA-20, 30, 60, 120, HX-620, D-310, 330 (Nippon 25 Kayaku Co., Ltd.), Aronix M-210, 215, 315, 325 (Toagosei Co., Ltd.), and A-MPD (Shin-Nakamura Chemical Co., Ltd.).

It is desirable that the poly-functional monomer is included in the composition of the present 30 invention as the component (B) in an amount of 0.1-10 wt%, and especially 0.5-5 wt%. If the proportion of the

component (B) is too small, the breaking strength of the resulting cured products is low. If this proportion is too large, the modulus of elasticity of the cured products is so high that elongation is decreased. Such 5 a product is not suitable as a primary coating material for optical fibers.

Component (C)

A monomer having one polymerizable vinyl 10 group and a molecular weight of 1,000 or less, preferably 70-800, is given as a typical example of the monomer having a polymerizable unsaturated group used as the component (C) in the present invention. Although there are no specific restrictions to the form of 15 polymerizable vinyl group, a form of (meth)acryloyl group such as an N-vinyl group, (meth)acrylamide group, vinyl ether group, or vinyl ester group, is given as an example. Of these, a form of (meth)acryloyl group is particularly preferred.

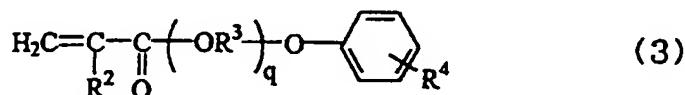
20 The component (C) functions as a reactive diluent in the composition of the present invention. Therefore, it is desirable for the component (C) to be a liquid at room temperature. It is possible to adjust viscosity of the composition and modulus of elasticity 25 of the cured products obtained from the composition by suitable selection of the types and amount of the compound, which is used as the component (C). When two or more compounds are used as the component (C), the mixture of these compounds only has to be liquid.

30 The following monomers are given as specific examples of the compounds used as component

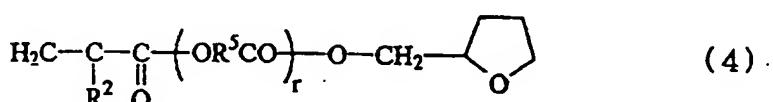
(C) :

2-hydroxyethyl (meth) acrylate,
2-hydroxypropyl (meth) acrylate,
2-hydroxybutyl (meth) acrylate, methyl (meth) acrylate,
5 ethyl (meth) acrylate, propyl (meth) acrylate,
isopropyl (meth) acrylate, butyl (meth) acrylate,
amyl (meth) acrylate, isobutyl (meth) acrylate,
t-butyl (meth) acrylate, pentyl (meth) acrylate,
isoamyl (meth) acrylate, hexyl (meth) acrylate,
10 heptyl (meth) acrylate, octyl (meth) acrylate,
iso-octyl (meth) acrylate, 2-ethylhexyl (meth) acrylate,
nonyl (meth) acrylate, decyl (meth) acrylate,
iso-decyl (meth) acrylate, undecyl (meth) acrylate,
dodecyl (meth) acrylate, lauryl (meth) acrylate,
15 octadecyl (meth) acrylate, stearyl (meth) acrylate,
tetrahydrofurfuryl (meth) acrylate,
butoxyethyl (meth) acrylate, ethoxydiethylene glycol
(meth) acrylate, benzyl (meth) acrylate,
cyclohexyl (meth) acrylate, phenoxyethyl (meth) acrylate,
20 polyethylene glycol mono (meth) acrylate, polypropylene
glycol mono (meth) acrylate, methoxyethylene glycol
(meth) acrylate, ethoxyethyl (meth) acrylate,
methoxypolyethylene glycol (meth) acrylate,
methoxypolypropylene glycol (meth) acrylate,
25 dicyclopentadienyl (meth) acrylate,
dicyclopentanyl (meth) acrylate,
dicyclopentenyl (meth) acrylate,
tricyclodecanyl (meth) acrylate, isobornyl (meth) acrylate,
bornyl (meth) acrylate, diacetone (meth) acrylamide,
30 isobutoxymethyl (meth) acrylamide, N-vinylpyrrolidone,
N-vinylcaprolactam, N-vinylformaldehyde,

N,N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide,
 dimethylaminoethyl (meth)acrylate,
 diethylaminoethyl (meth)acrylate,
 7-amino-3,7-dimethyloctyl (meth)acrylate,
 5 N,N-diethyl (meth)acrylamide,
 N,N'-dimethylaminopropyl (meth)acrylamide,
 (meth)acryloyl morpholine, hydroxybutyl vinyl ether,
 lauryl vinyl ether, vinyl ethers such as cetyl vinyl
 ether, 2-ethylhexyl vinyl ether, maleic acid esters,
 10 fumaric acid esters, compounds shown by the following
 formulas (3) - (5) :



wherein R^2 is a hydrogen atom or methyl group, R^3 is an
 alkylene group having 2-6, preferably 2-4, carbon
 15 atoms, R^4 is a hydrogen atom or an alkyl group having 1-
 12, preferably 1-9, carbon atoms, and q is an integer
 of 0-12, preferably 1-8,



wherein R^2 is the same as defined in the formula (3), R^5
 20 is an alkylene group having 2-8, preferably 2-5, carbon
 atoms, and r is an integer of 1-8, and preferably 1-4,
 and

EXAMPLES

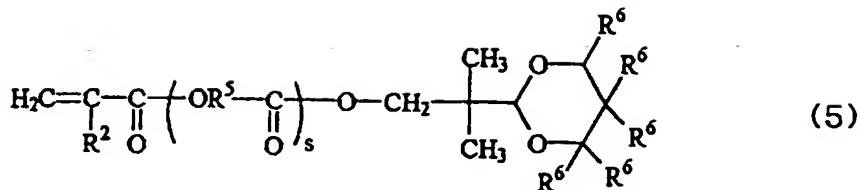
The composition of the present invention will now be described specifically by way of examples. In the following examples, "part(s)" means "part(s) by weight" unless otherwise indicated.

Synthetic Example 1Synthesis of polymers for component (A)

A reaction vessel equipped with a stirrer was charged with 4.07 g of tolylene diisocyanate (containing 97.5 wt% or more 2,4-isomer and 2.5 wt% or less 2,6-isomer), 59.3 g of a ring-opening copolymer of ethylene oxide and tetrahydrofuran with a number average molecular weight (hereinafter abbreviated as Mn) of 4,000, 0.02 g of 2,6-di-t-butyl-p-cresol, and 0.007 g of phenothiazine. The mixture was cooled with ice to 10°C or below while stirring. When the temperature was 10°C or below, 0.08 g of dibutyl tin dilaurate was added and the mixture was stirred for two hours while maintaining the temperature at 20-30°C.

Then, 0.33 g of γ -mercaptopropyltrimethoxysilane (trademark: SH6062, manufactured by Toray-Dow Corning Silicone Co., Ltd.), which is a silane coupling agent, was added and the mixture was stirred for one hour at 40-50°C. Next, 1.15 g of 2-hydroxyethylacrylate was added and the mixture was stirred for 30 minutes at 45-55°C.

0.13 g of methanol was added to the reaction solution, followed by stirring for 4 hours at 55-60°C.



wherein R^2 and R^5 are the same as respectively defined in the formulas (3) and (4), a plurality of R^6 independently indicates a hydrogen atom or methyl group, and s is an integer of 1-15.

5 As specific examples of the compound shown
by the formula (3), nonylphenol EO-modified (8 mole
modified) acrylate, phenol EO-modified (4 mole
modified) acrylate, nonylphenol EO-modified (4 mole
modified) acrylate, nonylphenol PO-modified (2.5 mole
modified) acrylate, nonyl phenol EO-modified (1 mole
modified) acrylate, and phenol EO-modified (2 mole
modified) acrylate are given. Here, "EO-modified" means
"modified with ethylene oxide" and "PO-modified" means
"modified with propylene oxide".

15 The compounds described above may be used either individually or in combinations of two or more.

Of the above-described compounds, it is desirable for the component (C) to include an N-vinylactam such as N-vinyl- ϵ -caprolactam (hereinafter described as N-vinylcaprolactam), and the like. In this case, the proportion of the N-vinylactams in component (C) is from 3-20 wt%, and preferably 3-15 wt%. N-vinylcapralactam is preferred.

Inclusion of a compound with an alicyclic structure is desirable for the component (C) to increase water resistance, hot water resistance, acid

resistance, and alkali resistance of the cured products, thus ensuring long-term reliability of the products. As examples of such monomers having an alicyclic structure, isobornyl (meth)acrylate,
5 dicyclopentenyl (meth)acrylate,
tricyclodecanyl (meth)acrylate,
cyclohexyl (meth)acrylate,
tricyclodecanedimethanoldi (meth)acrylate, and the like are given. Of these, isobornyl acrylate and
10 tricyclodecanedimethanoldiacrylate are preferred.

A combined use of the above-mentioned N-vinyl lactam and the compound having an alicyclic structure as the component (C) is given as a preferred embodiment.

15 These compounds for the component (C) are commercially available under the trademarks such as Aronix M-102, M-111, M-113, M-114, M-117 (Toagosei Co., Ltd.), KAYARAD TC110S, R629, R644 (Nippon Kayaku Co., Ltd.), and Viscoat 3700 (Osaka Organic Chemical
20 Industry Co., Ltd.).

It is desirable that the component (C) be incorporated in the composition of the present invention in an amount of 20-70 wt%, and preferably 25-55 wt%.

25 Component (D)

The following compounds are given as examples of radiation active initiators which are used as component (D) in the composition of the present invention: 1-hydroxycyclohexyl phenyl ketone, 2,2-
30 dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine,

carbazole, 3-methylacetophenone,
4-chlorobenzophenone, 4,4'-dimethoxybenzophenone,
4,4'-diaminobenzophenone, Michler's ketone, benzoin
propyl ether, benzoin ethyl ether, benzyl methyl ketal,
5 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one,
2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanethone,
diethylthioxanthone, 2-isopropylthioxanthone,
2-chlorothioxanthone, 2-methyl-1-[4-
(methylthio)phenyl]-2-morpholino-propan-1-one, 2,4,6-
10 trimethylbenzoyl diphenylphosphine oxide, and bis(2,6-
dimethoxybenzoyl)-2,4,4,-trimethylpentylphosphine
oxide. These compounds may be used either individually
or in combinations of two or more. Among these, 2,4,6-
trimethylbenzoyldiphenylphosphine oxide, bis(2,6-
15 dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide,
and 1-hydroxycyclohexylphenyl ketone are particularly
preferred.

The following can be given as commercially
available products of the component (D): IrgacureTM 184,
20 651, 500, 907 (Ciba Specialty Chemicals Co., Ltd.),
Lucirin TPOTM LR8728, Lucirin TPO LR8953X (BASF),
DarocureTM 1116, 1173 (Ciba Specialty Chemicals Co.,
Ltd.), and UbecrylTM P36 (UCB Co.).

These compounds for the component (D) may
25 be used either individually or in combinations of two
or more.

The proportion of the component (D) used in
the composition of the present invention is usually
0.1-10 wt%, and preferably 1-5 wt%.

30 A photosensitizer can be used together with
the radiation-active initiator of the component (D) as

required. As examples of the photosensitizers, triethylamine, diethylamine, N-methyldiethanoleamine, ethanolamine, 4-dimethylaminobenzoic acid, 4-ethyl dimethylaminobenzoate, 4-isoamyl dimethylaminobenzoate, 5 and commercially available products such as Ubecryl™ P102, 103, 104, 105 (UCB Co.), and the like can be given.

Other components

10 Additives other than the above-mentioned components (A) to (D) may be optionally added to the composition of the present invention. Included in such additives are antioxidants, UV absorbers, light stabilizers, silane coupling agents, aging preventives, 15 thermal polymerization inhibitors, leveling agents, coloring matters, surfactants, preservatives, plasticizers, lubricants, solvents, fillers, wettability improvers, coating surface improvers, and the like. As the antioxidants, for example, phenol-type 20 antioxidants, organic sulfur-type antioxidants, and the like are given. These are commercially available under the trademarks Irganox 1010, 1035, 1076, and 1222 (Ciba Specialty Chemicals Co., Ltd.), and the like.

As the above-mentioned UV absorbers, 25 benzotriazole-type UV absorbers, and the like can be given. As commercially available UV absorbers, Tinuvin™ P, 234, 320, 326, 327, 328, 213 (Ciba Specialty Chemicals Co., Ltd.), Sumisorb™ 110, 130, 140, 220, 250, 300, 320, 340, 350, 400 (Sumitomo Chemical 30 Industries Co., Ltd.), and the like can be given.

As examples of the above-mentioned light

stabilizers hindered amine-type light stabilizers and the like can be given. As commercially available products, Tinuvin™ 292, 144, 622LD (Ciba Specialty Chemicals Co., Ltd.), Sanol™ LS-770, 765, 292, 2626, 5 1114, 744 (Sankyo Co., Ltd.), and the like can be given.

As examples of the above-mentioned silane coupling agents, γ -aminopropyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, and 10 γ -methacryloxypropyltrimethoxysilane, as well as commercially available products under the trademarks SH6062, SZ6030 (Toray-Dow Corning Silicone Co., Ltd.), KBE903, KBM803 (Shin-Etsu Silicone Co., Ltd.), and the like can be given.

15 As examples of the above-mentioned aging preventives, phenol-type aging preventives, allyl amine-type aging preventives, and ketone amine-type aging preventives, as well as commercially available products under the trademarks Antigene W, S, P, 3C, 6C, 20 RD-G, FR, AW (Sumitomo Chemical Industries Co., Ltd.), and the like can be given.

The composition of the present invention can be prepared by blending the above-mentioned components (A) to (D) and the optional components at 25 appropriate proportions.

The viscosity (at 25°C) of the composition of the present invention is in the range of 1,000-20,000 cP, and preferably 1,500-15,000 cP, to ensure excellent coatability to optical fibers.

Cured products

The composition of the present invention is curable by irradiation with rays of an appropriate wavelength, suitable radiation includes infrared radiation, visible rays, ultraviolet radiation, α -rays, β -rays, γ -rays, and the like. When ultraviolet radiation is used (which is preferred), for example, the composition can be cured at an irradiation dose of 50 J/cm² or more. If the irradiation dose is 50 mJ/cm² or 10 more, preferably 100 mJ/cm² or more, the cured products exhibit a high breaking strength and a small amount of light transmission loss, in spite of a low modulus of elasticity. Generally, irradiation with 2 J/cm² less is preferred, and 1 J/cm² or less is more preferred.

Among the cured products obtained from the composition of the present invention by irradiation of ultraviolet light at a dose of 1 J/cm² in air atmosphere, those having (1) a secant modulus defined by the JIS K 7127 of 0.15 kg/mm² or less and (2) a tensile breaking strength, defined by the JIS K 7127, of 0.15 kg/mm² or more exhibit superior workability when the coating is to be stripped from optical fibers, without leaving any residue on the fibers. Because such a coating material provides an advantage of easy optical fiber joining work, the material is ideal for use as a primary coating for optical fibers. It is preferred to have cured products having a secant modulus of 0.12 kg/mm² or less. It is preferred to have cured products having a tensile breaking strength of 30 0.18 kg/mm² or more, in particular 0.21 kg/mm² or more.

In addition, the cured products obtained by irradiation with ultraviolet lights under the same conditions as mentioned above, those having a total of two or more peaks or shoulders in the temperature range from -50°C 5 to +35°C temperature dependency curve obtained from the loss tangent from temperature dependency measurement of dynamic viscoelasticity ratio, particularly, those having (a) at least one shoulder or peak in the temperature range from -50°C to -20°C and (b) at least 10 one shoulder or peak in the temperature range from -20°C to +35°C exhibit exceptionally superior workability when the coating is stripped from optical fibers. Such a product is especially suitable as a primary coating material for optical fibers. Cured products satisfying 15 both the above-mentioned requirements (1) and (2) at the same time, but having only one peak or shoulder in the temperature range from -50°C to +35°C, exhibit somewhat inferior workability in coating removal from optical fibers as compared with those having two or 20 more peaks or shoulders. Such cured products remain superior when compared with conventional primary coating material, and thus can be suitably used as a primary coating material for optical fibers.

25 Utility

In addition to a coating material for optical fibers (particularly a primary coating material), the composition of the present invention is useful as a paint, surface reforming agent, printing 30 ink, and the like.

The reaction was terminated when the residual isocyanate content was reduced to 0.1 wt% or less, thereby obtaining a liquid urethane acrylate polymer of the component (A) with a Mn of 8,327.

5

Examples 1-7, Comparative Examples 1-2

10 g of laurylacrylate (component (C)), 17 g of nonylphenol EO-modified (4 mole modified) acrylate (trademark: M113, manufactured by Toagosei Co., Ltd., component (C)), 5 g of N-vinylcaprolactam (component (C)), 0.8 g of Irganox 1035 as an antioxidant, 2 g of 2,4,6-trimethylbenzoyl diphenylphosphine oxide, and 0.15 g of diethylamine were added to 65 g of the liquid urethane acrylate polymer (component (A)) which was obtained in the Synthetic Example 1. The mixture was stirred while maintaining the temperature at 50-60°C until a transparent homogeneous liquid (resin solution I) was obtained. Mixtures of 100 parts of the resin solution I and poly-functional monomers shown in Table 1 or, in the case of Comparative Examples, no monomer, or laurylacrylate instead of the poly-functional monomers, in the amount shown in Table 1, respectively, were stirred for 3 hours while maintaining the temperature at 50-60°C, thereby obtaining compositions for Examples 1-7 and Comparative Example 2. The viscosity of the resulting compositions at 25°C was measured using a Brookfield type viscometer. The results are shown in Table 1, which indicates all compositions have a viscosity in the range from 5,000 to 6,000 cP.

The resin solution I was used as is without adding a poly-functional monomer as the composition for Comparative Example 1.

5 TABLE 1

	(B) Poly-functional monomer (parts)	Viscosity (cp/25°C)
Example 1	1,6-Hexanediacylate (0.8)	5500
Example 2	Triethylene glycol diacrylate (3.0)	5500
Example 3	1,6-Hexanediol diacrylate (1.5)	5500
Example 4	1,9-Nonanediol diacrylate (3.0)	5400
Example 5	Triethylene glycol diacrylate (1.0)	5500
Example 6	Tricyclodecanedimethanol diacrylate (3.0)	5400
Example 7	Triethylene glycol diacrylate (2.0)	5500
Comparative Example 1	-	5500
Comparative Example 2	Laurylacrylate (2.5)	5400

Each liquid composition thus obtained in the Examples or Comparative Examples was applied to a sheet of glass using an applicator for producing a coating with a

10 thickness of 250µm. The coating was irradiated with ultraviolet light from a 3.5 KW metal halide lamp (SMX-3500/F-OS, manufactured by ORC Co., Ltd.) at a dose of

1 J/cm² in air to obtain a cured coating with a thickness of about 200µm. The coating was conditioned at 23°C and 50% RH (relative humidity) for 12 hours and cut into strips with a width of 0.3 cm. These strips 5 were used as test specimens to measure the temperature dependency of loss tangent. Similar strips with a width of 0.6 cm were prepared as test specimens to measure modulus of elasticity and breaking strength. The results are shown in Table 2. In addition, 4-core 10 ribbons were prepared to evaluate ease of coating removal in one operation. The results are shown in Table 2.

Measurement of modulus of elasticity

15 Secant modulus was measured according to JIS K7127 at a bench mark distance of 25 mm and a pulling rate of 1 mm/minute.

Measurement of breaking strength

20 Tensile breaking strength was measured according to JIS K7127 at a bench mark distance of 25 mm and a pulling rate of 50 mm/minute under the conditions of 23°C and 50% RH.

25 Temperature dependency of loss tangent

Dynamic viscoelasticity was measured using RHEOVIBRON MODEL RHEO-1021 (control unit) and RHEOVIBRON MODEL DDV-01FP (measuring unit) manufactured by Orientech Co., Ltd. at a heating rate of 2°C/min, 30 bench mark distance of 30 mm, vibration frequency of 35

Hz, vibration swing of 10 μ m, and a temperature range from -100 $^{\circ}$ C to 100 $^{\circ}$ C.

Evaluation of ease of coating removal from optical

5 fibers

A four-core ribbon was nipped with a hot stripper S-214, manufactured by FURUKAWA ELECTRIC CO., LTD., for about 5 minutes at a temperature range of 85 \pm 2 $^{\circ}$ C. Glass core fibers were extracted from the 4-core 10 ribbon to observe remains of the primary coating on extracted glass fibers. The coating removability was rated as "Excellent" when there were no remains of the primary coating material left on the surface of the glass fiber, "Good" when there was a small amount of 15 remains, and "Bad" when the remains are significant.

TABLE 2

	Secant modulus (kg/mm ²)	Tensile strength at break (kg/mm ²)	Temperature at which loss tangent exhibits a peak or shoulder (°C)	Coating removability
Example 1	0.05	0.24	-11	Good
Example 2	0.07	0.15	0; -44	Good
Example 3	0.06	0.48	5; -40	Excellent
Example 4	0.07	0.42	7; -42	Excellent
Example 5	0.06	0.37	1; -45	Excellent
Example 6	0.08	0.34	8; -40	Excellent
Example 7	0.10	0.28	4; -46	Excellent
Comparative Example 1	0.04	0.06	2.7	Bad
Comparative Example 2	0.04	0.05	-7	Bad

As can be seen from Table 1, the compositions of Examples 1-7 have a viscosity of a 5 desirable range as a primary coating for optical fibers. The following findings are obtained from the results shown in Table 2.

The cured product of Example 1 showed a high tensile breaking strength of 0.24 kg/mm², although 10 the secant modulus was low (0.05 kg/mm²). This cured product exhibited only one peak in the loss tangent temperature dependence curve. There were no other peaks or shoulders except for that one.

The composition of Example 2 represents the composition having a tensile strength at break of 0.15 kg/mm²; the loss tangent temperature dependence curve had one peak and one shoulder. Example 3 has one peak at 5°C and one shoulder at -40°C as shown in Figure 1. With regard to the cured products made from the compositions of Examples 3 to 7, although the secant modulus was low (0.06-0.10 kg/mm²), the products exhibited high tensile strength at break of 0.28-0.48 kg/mm². In addition, the loss tangent temperature dependence curves of these cured products showed one peak or shoulder in the temperature range from -50°C to -20°C and another peak or shoulder in the temperature range from -20°C to +35°C. All cured products made from the resin compositions of the Examples 1 to 7 showed favorable coating removability from optical fibers. On the other hand, the cured products made from the compositions of Comparative Example 1 and Comparative Example 2 which do not contain a poly-functional monomer showed a low secant modulus and also a low tensile breaking strength. These products showed only one peak in the loss tangent temperature dependence curve (for example, the products of the Comparative Example 2 had only one peak at -10°C, as shown in Figure 2). In the evaluation of coating removability, the primary coating made from the compositions of Comparative Examples left a significant amount of remains on optical fibers.

Effect of Invention

The radiation curable composition of the present invention possesses favorable viscoelasticity and exhibits moderate resistance and deformation

- 5 against external forces. Because of this, when used as a coating material, particularly a primary coating material, for optical fibers the products have a high breaking strength, while exhibiting a low modulus of elasticity, and showing superior light transmission
- 10 characteristics with only a small amount of light transmission loss. In addition, removal of coating from optical fibers can be performed with extreme ease when optical fibers are joined together.

CLAIMS

1. A radiation curable resin composition comprising:
 - (A) a polymer containing polymerizable unsaturated groups in an average amount of 1.2-4 per one molecule, a urethane bond in a molecular chain, and having a number average molecular weight from 3,000 to 30,000,
 - (B) a poly-functional monomer having two or more polymerizable unsaturated groups,
 - (C) a monomer having one polymerizable unsaturated group, and,
 - (D) a radiation active initiator,wherein the compositions upon curing of 1 J/cm² in air, has a secant modulus of 0.15 kg/mm² or less and a tensile strength of 0.15 kg/mm² or more.
2. The radiation curable resin composition according to claim 1, which composition upon cure can produce a cured product having a viscoelasticity curve characterized by having a total of at least one peak and at least one shoulder, or at least two peaks in a temperature range from -50°C to +35°C in a temperature dependency curve of loss tangent.
3. The radiation curable resin composition according to claim 2, wherein the cured product has at least one peak or shoulder in a temperature range from -50°C to -20°C and at least one peak or shoulder in a temperature range from -20°C to +35°C in the temperature dependency curve of loss tangent.

4. A radiation curable resin composition according to any one of claims 1-3 where in the composition comprises:

5 (A) 25 to 75 wt% of a polymer containing polymerizable unsaturated groups in an average amount of 1.2-4 per molecule, a urethane bond and a polyoxyalkylene structure in a molecular chain, and having an average molecular weight from 3,000 to 30,000,

10 (B) 0.1 to 10 wt% of a poly-functional monomer having 2 to 6 polymerizable unsaturated groups,

(C) 20 to 70 wt% of a monomer having a one polymerizable unsaturated group, and

(D) 0.1 to 10 wt% of a radiation-active 15 initiator.

5. The composition according to any one of claims 1-4 wherein the polymer (A) possesses an average of 1.5-2.5 polymerizable unsaturated groups per molecule.

20 6. The composition according to any one of claims 1-5 wherein the whole or a portion of the main chain of the polymer (A) is a polyether polyol-type urethane acrylate polymer.

7. The composition according to any one of claims 1-25 6 wherein the component (B) is selected from the group consisting of diacrylate compounds and triacrylate compounds having a molecular weight of 800 or less.

8. The composition according to any one of claims 1-30 7 wherein the component (B) is selected from the group consisting of 1,6-hexanedioldiacrylate,

1,9-nonenediolacrylate, triethylene glycol diacrylate, tricyclodecanedimethanol diacrylate, and trimethylolpropane alkoxytriacylate.

9. The composition according to any one of claims 1-
5 wherein the component (C) has a molecular weight of 100-1000.
10. The composition according to any one of claims 1-
9 wherein the component (C) includes N-vinylactams.
- 10 11. The composition according to any one of claims 1-
10 wherein the component (C) includes N-vinylactams and monomers having an alicyclic structure.
12. The composition according to any one of claims 1-
15 11 having a viscosity of 1,000-20,000 cP at 25°C.
13. An optical fiber coated with a primary coating in uncured form is a composition according to any one of claims 1-12.

1/2

Figure 1

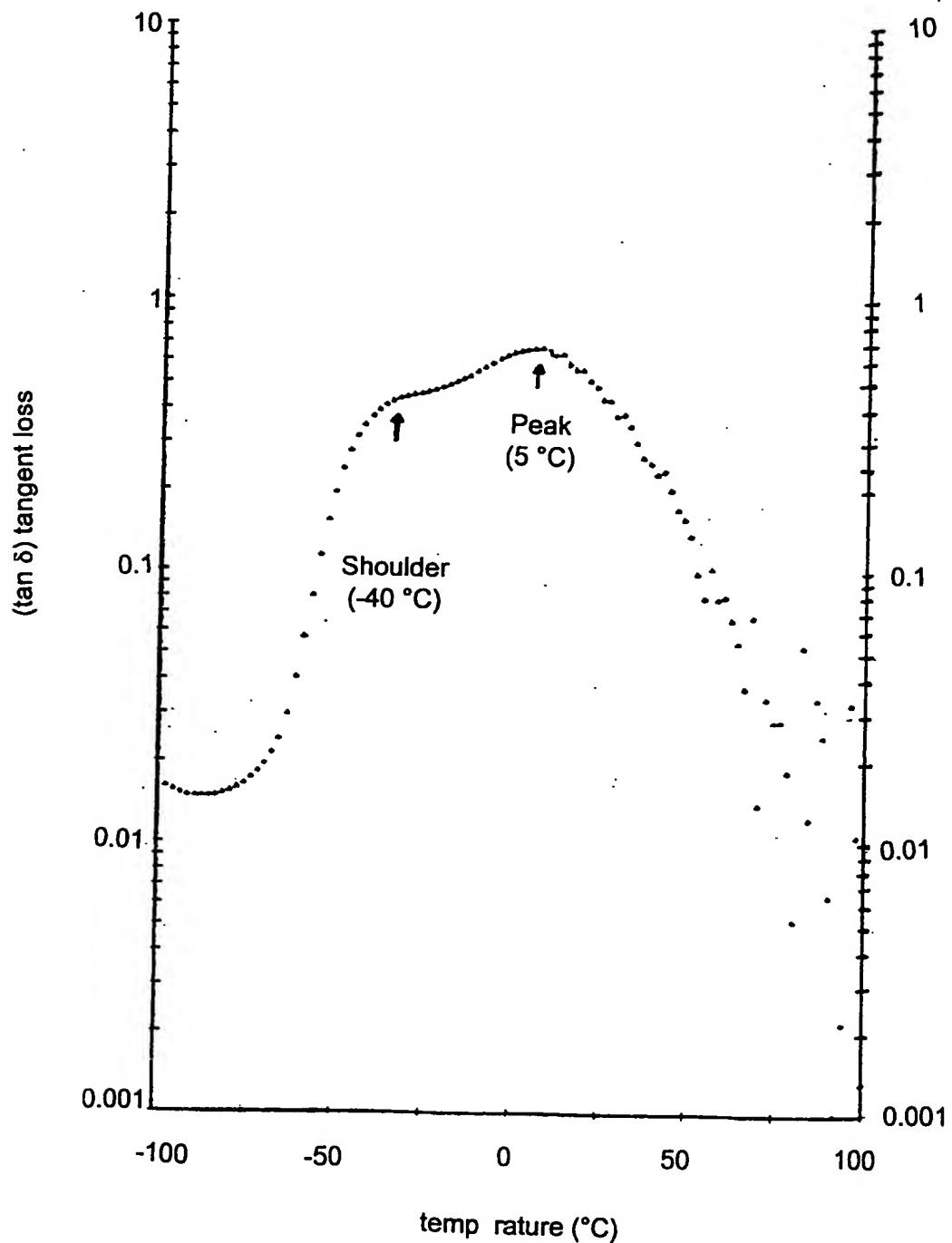
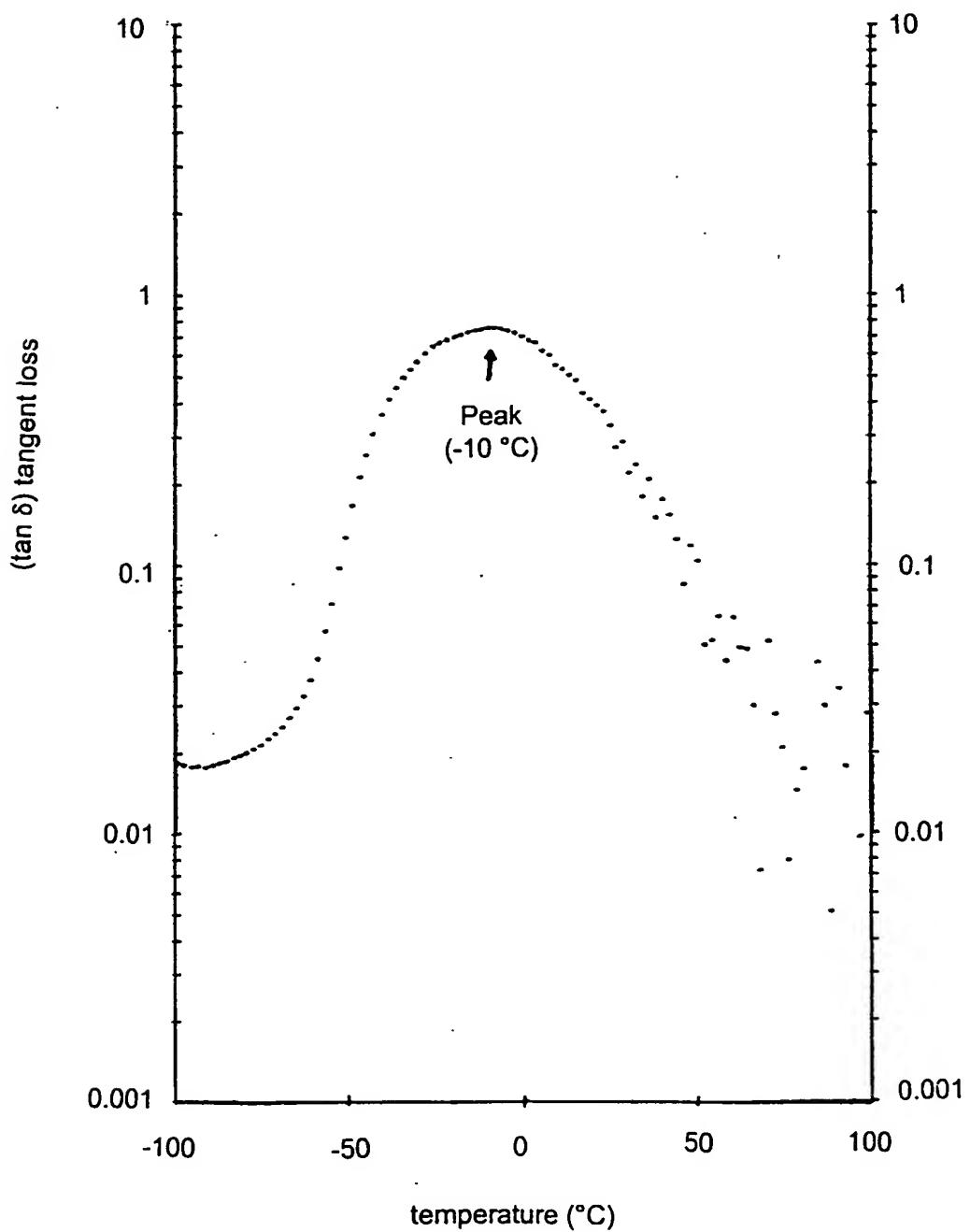


Figure 2



INTERNATIONAL SEARCH REPORT

Int'l	Application No
	PCT/NL 99/00215

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08F290/14 C08F290/06 C09D4/06 C03C25/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C08F C09D C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 4 932 750 A (ANSEL ROBERT E ET AL) 12 June 1990 (1990-06-12) claim 1 -----	1-13
X	EP 0 407 004 A (BORDEN INC) 9 January 1991 (1991-01-09) claims 1,3-6 -----	1-13
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
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 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 "&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Int. Search Application No

PCT/NL 99/00215

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Jpnal Application No

PCT/NL 99/00215

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